Internal Correspondence

MARTIN MARIETTA ENERGY SYSTEMS, INC.

November 9, 1989

W. R. Golliher

Technical Study of the Radionuclides Issues Related to the Operation of the Oak Ridge Mixed Waste Incinerator (ORMWI)

Attached is my evaluation of the radionuclides related issues connected with the operation of the ORMWI. The following subjects were examined:

- Review of ORMWI NESHAP limits for radionuclides
- Need for additional data
- Distribution of impurities between air, blowdown water, and ash, and
- Chlorine-36 rationale.

I recommend the following actions be taken:

- Determine the uranium distribution to the stack, scrubber water, and ash as soon as possible.
- The NESHAP feed limits may need to be renegotiated with the regulators.
- Improve analytical procedures to obtain maximum practical sensitivity and discrimination between radionuclides.

Should you have any questions or comments on the attached study or need further details, please let me know.

R W Anderson

R. W. Anderson, K-1006, MS-7272 (4-9938)

RWA:cap

Attachment

APPROVAL FOR RELEASE

Document: # **Unnumbered** ; Date 11/9/89 ;

Title/Subject 2-pg ltr (Anderson to Golliher) & 16-pg rpt, "TECHNICAL STUDY OF THE RADIONUCLIDES ISSUES RELATED TO THE ORMWI"

Approval for unrestricted release of this document is authorized by the Oak Ridge K-25 Site Classification and Information Control Office, Martin Marietta Energy Systems, Inc., PO Box 2003, Oak Ridge, TN 37831-7307.

K-25 Classification & Information Control Officer — Date 1/26/93

#76

Internal Correspondence

MARTIN MARIETTA ENERGY SYSTEMS, INC.

1989 NOV 15 PM 8:13

November 9, 1989

W. R. Golliher

Technical Study of the Radionuclides Issues Related to the Operation of the Oak Ridge Mixed Waste Incinerator (ORMWI)

Attached is my evaluation of the radionuclides related issues connected with the operation of the ORMWI. The following subjects were examined:

- Review of ORMWI NESHAP limits for radionuclides
- Need for additional data
- Distribution of impurities between air, blowdown water, and ash, and
- Chlorine-36 rationale.

I recommend the following actions be taken:

- Determine the uranium distribution to the stack, scrubber water, and ash as soon as possible.
- The NESHAP feed limits may need to be renegotiated with the regulators.
- Improve analytical procedures to obtain maximum practical sensitivity and discrimination between radionuclides.

Should you have any questions or comments on the attached study or need further details, please let me know.

R W Anderson

R. W. Anderson, K-1006, MS-7272 (4-9938)

RWA:cap

Attachment

cc: M. L. Ambrose
W. J. Armento
T. A. Bowers
W. D. Bostick
J. T. Bradbury
D. H. Bunch
E. E. Clark
H. T. Conner, Jr.
L. V. Gibson
R. L. Jolley
C. R. Kirkpatrick
W. C. McWhorter
A. L. Rivera
T. O. Rogers
T. L. Rucker, SAIC
S. P.N. Singh
RWA File

AN EVALUATION OF THE RADIONUCLIDES RELATED ISSUES PERTAINING TO THE OPERATION OF THE OAK RIDGE MIXED WASTE INCINERATOR

By

Roger W. Anderson
Oak Ridge Gaseous Diffusion Plant
Oak Ridge, Tennessee

November 9, 1989

REVIEW OF ORMWI NESHAP LIMITS FOR RADIONUCLIDES

Present air pollution control requirements includes a list of 21 isotopes with maximum allowed annual quantities (MAQs) of feed to the Oak Ridge Mixed Waste Incinerator (ORMWI). These MAQs range from 14,600,000 μCi/yr for the beta emitter Tc-99 to 90 μCi/yr for the beta emitter Cl-36, and from 420,000 μCi/yr for all alpha-emitting uranium isotopes to 3 μCi/yr for Th-230, an alpha emitter. Problems associated with radioanalytical discrimination in mixtures containing very small amounts of certain isotopes in the presence of 10^5 times larger quantities of similar emitters will make it impossible to determine whether or not maximum allowed quantities of the trace isotopes have been exceeded. The National Emission Standards for Hazardous Air Pollutants (NESHAP) limits for trace elements such as Cl-36, I-131, S-35, Ca-45, Cr-51, Co-57, Zn-65, K-40, Cs-137, and Th-230 are so small that false positive values for isotope activity with apparent (but not real) noncompliance with feed limits are likely. Nine of the NESHAP feed limits average about 10^{-7} times the isotope concentrations in Schedule RHS 8-1, Table II, column 2 of Chapter 1200-2-5-0.08, and the average of six of these isotopes on the maximum annual feed list are less than 2.5% of anticipated Tc-99 plus H-3 beta activities. Therefore, the release of these isotopes will not pose a significant health threat in comparison to the release of uranium, Tc-99, and tritium isotopes.

To remedy this problem with isotopes which may be present in trace amounts in feed mixtures along with larger quantities of other isotopes, it is recommended that either: (a) rules be established for trace isotopes in mixtures similar to those employed by the NCRP or (b) higher limits be negotiated with the regulators for the amounts of those isotopes that can be detected in certain waste mixtures.

The above-mentioned NCRP rule states,[1] "....a radionuclide may be considered as being not present in a mixture if: (a) the ratio of the concentration of that radionuclide in the mixture (C_A) to the concentration limit for that radionuclide specified in Table II (MPC_A)

of Ref. 1 does not exceed 1/10 (i.e., $C_A/MPC_A \leq 1/10$) and (b) the sum of such ratios for all the radionuclides considered as being not present does not exceed 1/4, that is, $C_A/MPC_A + C_B/MPC_B + ... \leq 1/4$."

Therefore, application of this rule would permit the use of the MAQ limits in the current ORMWI NESHAP permit. The trace isotopes can then be batch-fed to the incinerator provided their concentrations in the feed are known. These concentrations can then be added to the annual permitted radionuclide loadings stipulated for the incinerator. When no known reason exists for the presence of an isotope in the incinerator feed, this isotope will not be analyzed for nor counted as being present.

If a rule similar to that employed by the National Committee for Radiation Protection (NCRP) is not acceptable to the regulators, new maximum allowable quantities of radionuclide feeds will have to be negotiated with regulators. In this case, it is recommended that the limit for trace beta emitting isotopes be 130,000 μCi/yr and for trace alpha emitters (such as Th-230) be 1000 μCi/yr so that the measured quantities of radionuclides reported whose analyses exceed these limits will actually be present. If the concentration of any beta emitter is less than 13,000 μCi/yr, it is recommended that this isotope not be considered as being present provided the sum of all the trace beta isotope activities when divided by 130,000 μCi/yr is less than 1/4. Similarly, Th-230 would not be considered as being present if its measured concentration was less than 100 μCi/yr, and the sum of all trace alpha activities when divided by 1000 μCi/yr was less than 1/4.

Table 1 gives recommended feed limits for various isotopes based upon experimentally observed emissions of elements or isotopes to air and scrubber water effluent.

Uranium

The NESHAP permit annual guideline for the incinerator vent stack emissions is 26.3% of the NESHAP uranium feed limit of 420,000 μCi/yr. This is about 200 times the nonoccupational NRC discharge limit for total soluble uranium in air, as given in Appendix 12B, Table II,

Column 1. During the period from November 18 to 28, 1988, 86.9 μCi of uranium were released from the K-1435 stack, as compared to an estimated 177 μCi of uranium feed and a background emission rate while burning natural gas of 0.11 μCi/hr. Based upon these data, 35.6% of the uranium fed was emitted from the stack. This removal efficiency is much lower than expected. If this removal efficiency is real, then for the permitted feed rate of uranium, the stack emission may exceed current NESHAP guidelines and could result in excessive radiation exposure to off-site personnel. Therefore, good data for uranium removal efficiencies by the incinerator and scrubber system are urgently needed.

During the November 22, 1988 air test, an average of 51.3% of the uranium fed entered the scrubber water. Most of the remainder may have ended up in the wet ash, but analyses were not obtained to prove this. In the future, analyses for ALL HAZARDOUS METALS AND RADIONUCLIDES need to be obtained for all feed materials and for all effluents including ash and water, scrubber blowdown water from both the quench and the ionizing wet scrubber, and air emissions.

Wastes with high concentrations of uranium radioactivity should probably only be fed to the rotary kiln until better data are available for uranium removal efficiencies.

Technetium-99

From January 1, 1989 to August 1989, Tc-99 air emission activities have been 4.46 times uranium emissions, and this will probably be typical of the incinerator waste feeds containing uranium from enrichment facilities. The NESHAP feed limit of 14,600,000 μCi/yr is probably too high when compared to average Tc-99 levels in materials planned for incineration. There is one exception, namely, if anion exchange resins having sorbed Tc-99 are burned in the incinerator. For 14,600,000 μCi/yr feed to the K-1435 mixed-waste incinerator, levels of Tc-99 in aqueous scrubber blowdown would average about 89.55% of the Central Neutralization Facility permit limit for aqueous Tc-99 discharge as given by Schedule RHS 8-1, Table II, Column 2, of Chapter 1200-2-5-0.08, and Tc-99 air emissions would average about 86.24% of the present NESHAP stack effluent annual guidelines. Tc-99 air emissions which are

dispersed and settle into the Clinch and Poplar Creek River basins will be washed into drinking water supplies and add to radioactive exposure which might cause radiation exposures above safe guideline units. Therefore, it is recommended that the NESHAP officials be petitioned to decrease the incinerator feed limit from 14,600,000 μCi/yr to 750,000 μCi/yr. This decrease would result in 99% probability that Fernald wastes stored in K-711 could be fed to the incinerator at a rate of 800 lb/hr for 305 days without exceeding the 750,000 μCi/yr feed limit. The average stack effluent with this feed would contain less than 4.43% of the present NESHAP stack effluent annual guideline. The average annual aqueous blowdown concentration for a feed rate of 750,000 μCi/yr to the rotary kiln would be about 4.6% of the NPDES permit limitation for radioactivity discharge from the CNF as given by Schedule RHS-8-1, Column 2 of Chapter 1200-2-5-0.08. This change may significantly decrease hazards from radioactivity to off-site personnel or the environment.

Other Radionuclides

A discussion of problems in analyzing for trace amounts of Cl-36, a beta emitter, in the presence of much larger activities of Tc-99, is given in Appendix A. Problems anticipated with analyses for Cl-36 and other radionuclides are the reason for the larger recommended feed limits for other radionuclides than are permitted by the current NESHAP feed limits. The lower value for I-125 takes into account the Nuclear Regulatory Commission (NRC) air discharge limits. This smaller recommended limit for I-125 also takes into account the short half-lives for I-125 and I-125m. Recommended values for the transuranics Th-228 through Pu-239 average about 500 times air discharge limits by the NRC because compounds of these elements will have low volatility and solubility, and recovery within the incinerator is expected to be very high with gas discharges being 0.5% or less of the input levels.

Carbon-14

The NESHAP C-14 feed limit of 138,000 μCi/yr is probably reasonable and adequate if C-14 from natural sources is not included with the feed. If natural sources are included, the C-14 limit will be too small.

the age at which a fuel source was formed and the formation process. However, variations in C-14 from natural sources will be small because each pound of carbon burned contributes only about 2.3×10^{-4} μCi of C-14 radiation.

Need for Additional Data

Adequate data for determination of whether or not most stored waste can be incinerated, and the distribution of radionuclides and toxic metals to air, water, and ash upon incineration have not been obtained for most wastes. Destruction and removal efficiencies for uranium are urgently needed to determine if the present NESHAP feed limit will result in excessive discharges of uranium to the atmosphere.

Incinerator Scrubber

The scrubber system requires modifications before resuming testing so that optimum pH levels can be obtained in each section of the scrubber, to improve the caustic feed response time so that: (1) when spikes of HCl are introduced after batchwise addition of chlorinated solids, caustic will be introduced rapidly enough to neutralize the acid spike, (2) to reduce caustic usage, and to obtain a steady state blowdown from the IWS system, and (3) decrease discharge of toxic metals from the stack. A report* has been written on necessary scrubber modifications. This includes a drawing showing the necessary changes.

Scrubber Liquid Treatment in CNF

Radioactivity in the outfall from CNF (011) must be reduced to levels as low as reasonably achievable (ALARA) and at a minimum, each discharge shall comply with the limitations in Schedule RHS 8-1, Table II, Column 2 of Chapter 1200-2-5. These limits are applicable where the discharge enters the receiving stream. The radioactivity limits will limit quantities of uranium, technetium, and other radioactive discharges. For 5% total uranium, the Column 2 values cited above limit uranium in scrubber blowdown to 3.04×10^{-5} μCi/mL or 1.73×10^{6} μCi/yr. This

*R. W. Anderson, Recommended Changes in the K-1435 Incinerator Scrubber, ORGDP-K/QT-309, November 1989.

translates to 6 mg total uranium per liter if the CNF conditions will not achieve a lower value by removal by precipitation. A value of 6 mg U/L of scrubber water blowdown corresponds to an average feed concentration of 107 ppm for 800 lb/hr of feed. A value of 6 mg U/L would be a reasonable maximum value for CNF based upon the solubility of hexavalent uranium in the concentrated scrubber blowdown solutions. Significantly lower values cannot be assured by pH adjustment. Ferrous iron may not be a strong enough reducing agent to convert the U^{+6} to the less soluble U^{+4}, but powdered iron metal or sulfite would be able to reduce the U^{+6} to achieve lower uranium solubilities.

Tc-99

Column 2 of Table II of chapter 1200-2-5 limits soluble Tc-99 to 3×10^{-4} μCi/mL (3×10^{5} pCi/L) which corresponds to 17.6 mg Tc-99/L. This is 125 times the average value for Tc-99 in the air test sump water. Pertechnate (TcO_4^-) is very soluble, and in 0.1 to 2.6 M sodium chloride at pH values from 7-9, $Tc(IV)O_2 \cdot H_2O$ has a solubility of (0.258 $\pm$ 0.099) μg/L.* This value is less than the permitted concentration of 17.6 μg Tc-99/L by a factor of 68. Therefore, if necessary, the concentration of both Tc-99 and uranium could be decreased with some difficulty below values given in Table II, Column 2 of Chapter 1200-2-5 by reduction under acidic conditions followed by pH adjustment to about 7.5 $\pm$ 0.5 with sufficient free calcium ion added to precipitate fluoride. Successful treatment might require addition of a sufficient surface area of seed crystals for $UO_2 \cdot 2H_2O$ and $TcO_2 \cdot nH_2O$ precipitation.

DISTRIBUTION OF IMPURITIES BETWEEN AIR, BLOWDOWN WATER, AND ASH

Analysis of feed, scrubber liquid, and ash from the October 21, 1988 air test, a previous solids waste burn on October 10-11, 1988, and

---

*R. E. Meyer, W. D. Arnold, F. I. Case, and G. D. O'Kelley, Thermodynamic Properties of Tc(IV) Oxides: Solubilities and the Electrode Potential of the Tc(VIII)/Tc(IV)-Oxide Couple, ORNL-6480 (NUREG/CR-5108), May 1988.

the August 8, 1988 NESHAP test have permitted estimates of distributions of fed components between air, water, and ash. Table 2 shows the fractional collection of specific impurities in scrubber liquid relative to the chlorine collection in scrubber liquid with the assumption that 100% of the chlorine fed to the incinerator ends up in the scrubber liquid for these three tests. Data in Table 2 illustrate that where the wastes were fed and the type of wastes influenced how much of the waste element ended up in the scrubber liquid. When Tc-99 and U were in the solids fed to the kiln, only 42 and 37%, respectively, of the impurity ended up in the scrubber liquid because of fallout of impurity into the ash pit by nonvolatile Tc and U in the solids. Aluminum phosphate and silicate present in the October 1988 test solids are nonvolatile, and only small amounts entered the scrubber, but aluminum present in the chlorinated organic was volatile and this was collected in the scrubber liquid. Ortho- and pyrophosphates are not volatile, but the organic soluble phosphate esters decompose or volatilize to give volatile phosphorous which is collected by the scrubbing liquid. Lead in the solids had about the same volatility as lead nitrate introduced with the aqueous liquid. Therefore, the lead is likely to end up in the scrubber liquids or in the stack emissions. Chromium had a relatively low volatility probably due to conversion of hexavalent to trivalent chromium at elevated temperatures, and nickel had the lowest volatility of all metal compounds in the wastes fed.

The low values for species in the scrubber effluent do not necessarily indicate that high values will be found in the stack because nonvolatile compounds can end up in the incinerator ash. As an approximation, if an impurity is present as a particulate, the amount of particulates escaping from the stack can be estimated from the scrubber solids concentration knowing that the scrubber particulate removal efficiency is rated as 97.3%. This scrubbing efficiency has been used to estimate distribution of elements to the stack and ash pit from scrubber collection efficiencies and from feed or total effluent in Table 3. For fluoride, lead, and the beryllium scrubber liquid, solid-

ash, ash-water, and gas-stack emission rates were measured as well as the feed rates.

These data indicate that most all of the volatile chlorides (such as calcium, boron, zinc, barium, and aluminum) end up in the scrubber liquid. Significant fractions of the very volatile beryllium and lead pass through the scrubber and enter the stack. A radioanalysis of stack effluent which was obtained before, during, and after the air test indicated that as much as 35.6% of the uranium passed through the scrubber to exit the stack as air emissions. Such poor uranium collection efficiency could have serious significance. The uranium activity of the effluent from the stack would exceed the permissible concentration in air for nonoccupational exposure by [(420,000 x 0.356)/(700) = 214] times* as given in Appendix 12B, Table II, Column 2 of ref. 2.

Dispersion of the stack effluent would undoubtedly decrease exposure to uranium, but drinking water contamination by blowdown water, and water runoff of deposited uranium needs to also be factored into the total human exposure to radioactive emissions from the incinerator. The uranium data for stack emissions as a percent of feed for the 10-day period of collection are quite uncertain because of uncertainties in uranium activities of the wastes fed to the incinerator.

Reliable data for uranium feed rates and emissions are urgently needed as soon as possible for several different types of waste feeds. OBTAINING A GOOD NUMBER FOR URANIUM DISTRIBUTION BETWEEN THE SCRUBBER, ASH PIT, AND STACK EFFLUENT SHOULD BE A PRIORITY ITEM DURING THE NEXT AIR TEST. Both radioactivity data for uranium and uranium concentrations should be measured for the feed, air emissions, scrubber blowdown, and ash. Stack samples for uranium and uranium activity should be collected during the period of steady state operation to obtain data for calculation of uranium scrubber collection efficiencies and air emissions.

---

*This figure does not consider dilution of the uranium activity by dispersion prior to exposure of nonoccupational personnel.

It is the author's opinion that after careful data have been collected and analyzed that stack emissions of uranium activity will be found to be only about 1.4% of the feed rate. This rate of emission should not result in excessive exposure of any plant personnel or off-site personnel to uranium activity.

Only about 2.0% of Tc-99 fed to the incinerator ended up as air emissions, and this should pose no hazard to on-site or off-site personnel since the μCi of Tc-99/mL of air emitted is only 0.1% of the value in Appendix 12B, Table II, Column 1, and the μCi of Tc-99/mL in the scrubber water effluent would only be 4.6% of the allowable nonoccupational exposure reported in Appendix 12B (Part 20, 25 FR 10914), Table II, Column 2, for an annual feed rate of 750,000 μCi of Tc-99. However, at the present permit rate of 14,600,000 μCi/yr, the scrubber water emissions would be 89.5% of the allowable nonoccupational exposure limit given in Appendix 12B, Table II, Column 2 for soluble Tc-99. Reduction to the +4 valence state with ferrous iron could result in suspended solids exceeding the allowable limit for Tc-99.

Expected Emissions of Toxic Metals

Expected emissions to air and water of metals and radionuclides cannot be estimated for most elements and isotopes because data have not been obtained for metal and isotope concentrations in all wastes to be incinerated, and the chemical nature of the compounds of these metals and isotopes has not been determined. Much lower emissions to water and air can be expected when contaminated wastes are fed only to the incinerator kiln, and not to the secondary combustion chamber, especially when the metal compounds formed by incineration are nonvolatile materials. In general, wastes having similar contaminant concentrations should be treated in campaigns to permit optimization of the incinerator and the CNF conditions to minimize waste discharges.

SUMMARY

In summary, the following actions need to be taken:

- Determine the uranium distribution to the stack, scrubber water, and ash as soon as possible.
- Either enter into negotiations with the regulators to accept the NCRP guidance with respect to the presence/absence of trace radionuclides in a mixture, or renegotiate new feed limits for trace radionuclides which are large enough so that the analytical data can prove feed limits have not been exceeded.
- Improve analytical procedures to obtain maximum practical sensitivity and discrimination between radionuclides.

REFERENCES

1. Patty's Industrial Hygiene and Toxicology, Third Rev. Ed., Vol. 1, General Principles, appendix 12B, "Permissible Concentrations in Air and Water," pp. 495-510, John Wiley and Sons, 1978.

2. Ibid., p. 508.

Table 1. Comparison of recommended feed limits with NESHAP K-1435 feed limits and nonoccupational air discharge limits by NRC

Recommended feed limits will allow incineration of stored wastes while remaining in compliance with current NESHAP air and NPDES and DOE discharge limits for aqueous waste. Air flow assumed: 17 ft/sec from stack or 2.0175×10^{14} mL/yr. Incinerator on stream 305 days/yr.

Parameter	NESHAP annual feed limit, μCi	Realistic recommended feed limit, μCi[b]	Appendix 12B,[c] Table II, Col. 1 nonoccupational air discharge limits[a] by NRC
Uranium (U_T)			
2.6% U-235	420,000	400,000	700[d] (1000)[e]
Technetium (Tc-99)	14,600,000	750,000	40,000,000
Tritium (H-3)	1,580,000	1,580,000	40,000,000
C-14	183,000	183,000	16,847,000
P-32	205,000	205,000	336,940
S-35	76,000	130,000	1,516,232
Cl-36	90	130,000	1,684,700
Ca-45	9,000	130,000	1,684,700
Cr-51	11,000	130,000	67,388,000
Co-57	920	240,000	1,684,700
Zn-65	460	130,000	673,880
I-125	291,0900	130,000	134,776
I-131	51,000	130,000	168,470
K-40	6,600	130,000	-
Cs-137	440	130,000	336,940
Th-230	3	1,000	13.5
Th-228	30	1,000	3.3
Th-232	1,110	1,110	13.5
Np-237	2,900	2,900	84
Pu-238	1,100	1,100	10
Pu-239	3,100	3,100	12

[a]Nonoccupational air limits in μCi/mL were multiplied by 2.0175×10^{14} mL/yr to derive annual limits from Appendix 12B data. Values given are above normal background limits and not total radioactivity limits.

[b]A radionuclide in a mixture is not considered present if (a) the concentration for that nuclide is less than 1/10 that in column 1 of Table II (i.e., $C_A/MPC_A \leq 1/10$) where MPC_A is the value given in column 1, and the sum of all ratios for nuclides not considered as present does not exceed 1/4.

[c]Patty's Industrial Hygiene and Toxicology, Third Revised Edition, Vol.1, General Principles, Appendix 12B, "Permissible Concentrations in Air and Water," pp. 495-510, John Wiley and Sons, 1978. Also given in DOE 5480.1, Chapter 2, 4-29-81, Attachment XI-1, pp. 1-16.

[d]Computed value for soluble uranium based on 0.03134 wt % U-234, 97.36 wt % U-238, and 2.63 wt % U-235.

[e]Calculated value for insoluble uranium.

Table 2. Fractional collection of the impurities in the incinerator feed by scrubber liquid assuming that 100% of the Cl is collected in the liquid

Ratio [(Element conc. in scrubber blowdown, mg/L)/(Mean conc. of element in feed, mg/kg)] divided by [(C) concentration in scrubber blowdown, mg/L)/Cl conc. in feed, mg/kg)]

Parameter	Fraction collected by scrubber liquid for 11-21-88 air test with organic, aqueous, and solid feeds	Est. fraction collected by scrubber liquid during 8-8-88 NESHAP test	Fraction collected by scrubber during 144 lb/hr burn of solid wastes on 10/10-11/88 clean liquids, solids only; weight basis
Cl	1.000	1.000	1.000
Tc-99	0.88	0.36	0.37
U(T)	0.27	-	0.10
F	0.464	-	-
Pb	0.307	-	0.40
Be	0.228	-	-
B*	1.63	0.56	-
Zn	11.2**	<0.74	0.024
P	0.712	0.0088	-
Al	0.932	2.89	0.0088
Cr	0.00753	0.084	0.0055
Ni	0.00732	<0.025	0.000009

*Boron was probably volatilized and lost from feed sample before analysis.

**With acidic organic feed, corrosion of galvanized steel increased zinc in blowdown.

Table 3. K-1435 average feed and blowdown concentrations and estimated scrubber efficiencies for October 21, 1988 air test

Feed parmeters	Feed* conc., μg/g	Blowdown conc. μg/g	Ratio blowdown to feed conc.	Percent of total feed or effluent** In liq. blowdown	In Ash	In stack
Cl	251,200	37,420	0.149	$99.93_e(188.2)_f$	0	0.072
Ca	873.4	132	0.151	$99.93_e(191.0)_f$	?~0	0.073 est.
Na*	1298	26,400	20.4	-	-	-
Tc-99	0.00231	0.000140	0.070	88_e	10_e	2.0_e
U(T)	128.6	5.23	0.0407	51.3	13.1(47.3)	35.6(1.4)
F	67,900	4700	0.0692	96.98_e	2.64_e	0.38_e
Pb	976	39	0.0400	$68.4_e(50.5)_f$	11.8_e	19.8_e
Be	1.915	0.070	0.036	86.4_e	3.2_e	10.4_e
B***	373.3	90	0.241	$(304.9)_f$	?	$(8.5)_f$
Zn****	4.341	7.23	1.67	$(2,111)_f$	?	?
Al	450	44.9	0.0998	$(126)_f$	(~0)	$(0.03)_f$
P	5000	381.1	0.0762	$(96.3)_f$	$(1.0)_f$	$(2.67)_f$
Sr	41	1.23	0.0301	$(38.0)_f$	$(61)_f$	$(1.05)_f$
Cu	40	1.43	0.0358	$(45)_f$	$(54)_f$	$(1.2)_f$
Si	4100	128	0.0312	$(39.4)_f$	$(60)_f$	$(1.09)_f$
Ba	6.4	0.62	0.097	$(122.4)_f$	?	$(3.4)_f$
Mn	42	0.30	0.0071	$(90)_f$	$(9.8)_f$	$(0.25)_f$
Fe	2800	14.6	0.00520	$(6.57)_f$	$(93)_f$	$(0.18)_f$
Cr	780	0.629	0.000806	$(1.018)_f$	$(99)_f$	$(0.028)_f$
Ni	530	0.311	0.000587	$(0.742)_f$	$(99)_f$	$(0.021)_f$

*Feed concentration basis weight does not include quench water. Only Ca and Na feeds include contribution from quench water. Na feed does not include NaOH feed.

**Subscript e refers to total effluent basis and f to feed basis. Various factors caused total effluent to exceed measured feed. Parentheses are estimates based on known scrubbing efficiency of 97.3%.

***Boron feed concentration is low due to volatilization loss during sample preparation before analysis.

****Corrosion of zinc from galvanized steel piping increased zinc concentration in system.

APPENDIX A. CHLORINE-36 RATIONALE

The NESHAP Cl-36 limit is much lower than necessary to protect the health and safety of people and the environment based upon comparison with tabulations of maximum permissible concentrations of radionuclides in air and water for nonoccupational exposures given in Appendix 12B (Part 20, 25 FR 10914) and NCRP Report No. 22. Table 1 compares NESHAP feed limits with air discharge limits derived from Appendix 12B, Table II, Column 1, and feed limits recommended by the author on the basis of feeds to be incinerated and safe levels for contaminants from these feeds in the incinerator gaseous and aqueous effluents.

The Cl-36 NESHAP feed limit of 90 μCi/yr is so low that in the presence of Tc-99, K-40, Cs-137, and Sr-90, the total beta activities is more than about 7 to 10 times the Cl-36 activity. Whether or not the Cl-36 fed to the incinerator is present at a level less than 90 μCi/yr cannot be determined with any degree of certainty using scintillation counting with beta energy discrimination, even if the true Cl-36 concentration is zero. The following factors contribute to the analytical problem.

- Beta emitters emit a spectrum of beta particles with energies from close to the isotopic decay energy down to zero so that the lower energy beta particles from different isotopes have energies which overlap. For example, for Cl-36 even though the maximum β^- particle energy is 709.5 keV, the average particle energy is 251.37 keV, which is less than the maximum β^- particle energy for Tc-99. This means that if both Cl-36 and Tc-99 were present at current NESHAP feed limits and if only beta particle disintegrations having energies greater than 217 keV were counted, and if 70% of Cl-36 and only 0.003% of Tc-99 disintegrations were counted, a calculated value for the Cl-36 activity of 8 $\pm$ 25 dpm/100 mL would be obtained from a single measurement. At least 12 similar measurements would

be required to establish that Cl-36 is probably present at the 95% confidence level.

- Potassium persulfate is employed to oxidize lower valent Tc ions to heptavalent pertechnate (TcO_4^-). Efficient separation of TcO_4^- from Cl^- and oxidized Cl anions is not possible because of similarity of distribution coefficients. Furthermore, persulfate reagent contains 0.012% of its potassium ions as a radioactive beta particle emitter, K-40, which has an average beta energy of 588.6 keV as compared to a maximum particle energy of 709.5 KeV for Cl-36. K-40 is also introduced by the scrubber caustic solutions and the makeup water. This K-40 is not distinguishable from Cl-36 radiation at the very low Cl-36 feed rate limit of 90 μCi/yr. Therefore, false positive values of Cl-36 greater than 90 μCi/yr are apt to be obtained even if Cl-36 is not present. Therefore, it is recommended that NESHAP regulators be requested to increase the permitted feed rate from 90 to 130,000 μCi/yr. With the 130,000 μCi/yr feed rate for Cl-36 and an average Tc-99 concentration corresponding to 150,000 μCi/yr and beta particle energy discrimination to exclude 99.7% of Tc-99 disintegrations, the expected experimental activity of 109 $\pm$ 2.5 dpm/ml is obtained for Cl-36 in the presence of an average Tc-99 of 150,000 μCi/yr.

The increase in the feed limit for Cl-36 from 90 to 130,000 μCi/yr would have no significant effects on hazards from radiochemical exposure from air or water. For an average chlorine DRE of 99.907%, annual air emissions would be only 0.00012 Ci/yr at a concentration of 5.9×10^{-13} μCi/mL as compared to 1×10^{-8} μCi/mL for nonoccupational exposure from Appendix 12B, Table II, Column 1. The corresponding value for scrubber blowdown at 29 gpm for 305 days would be about 2.7×10^{-6} μCi/mL as compared to 8×10^{-5} μCi/mL for the NPDES limit from Schedule RHS 8-1, Table II, Column 2, of Chapter 1200-2-5. It should be noted, however, that the level is high enough to require monthly isotope analyses to identify the nuclides present in the aqueous discharge.